

## EPR study of bis(methazolamidato) bipyridindiaquo-copper(II)

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*Received 18 February 1994, accepted 27 March 1995*

**Abstract** : Powder and single crystal EPR spectra of  $[\text{Cu}(\text{macm})_2(\text{Py})_2(\text{OH}_2)_2]$  compound suggest a tetragonal-octahedral symmetry of  $\text{Cu}^{2+}$  ion site with a small rhombic distortion. Characteristic EPR parameters are the following :  $g_{\parallel} = 2.27$ ;  $g_{\perp} = 2.06$ ;  $A_{\parallel} = 161.10^{-4} \text{ cm}^{-1}$ ;  $A_{\perp} = 21.10^{-4} \text{ cm}^{-1}$ . The bonding coefficients  $\alpha^2 = 0.79$ ,  $\beta^2 = 0.67$ ,  $\delta^2 = 0.75$ , indicate an appreciable covalent degree for both  $\sigma$  and  $\pi$  bonds. The angular dependence of the linewidth with  $g$  tensor orientation in the molecular frame are reported too.

**Keywords** : EPR, single crystal, metalloenzyme

**PACS Nos.** : 61.72.Hh, 76.30.Da, 87.64.Hd

EPR spectroscopy is widely used for the study of the structure of metalloenzymes and metalloproteins [1,2]. It provides information about the electronic structure of the metal ion and its surroundings, including the geometry and nature of the ligands [3].

It is known that sulphonamides cause an inhibition of the zinc metalloenzyme carbonic anhydrase [4]. The metal complexes having analogous methazolamide ([N(4-methyl-2-sulphamoyl- $\Delta^2$ -1,3,4-thiadiazolin-5-ylidene)], acetamide) (abbreviated as Hmacm) as a ligand are studied because the substitution of the N(thiadiazole) atom closest to the acetamide group probably hampers the coordination *via* the nitrogen atoms of the ring, a similar way to that observed in the active site of the metalloenzyme [5].

The  $[\text{Cu}(\text{macm})_2(\text{Py})_2(\text{OH}_2)_2]$  complex and their single crystals were prepared as previously reported [6]. X-ray structure of the complex shows that the copper(II) ion is surrounded by two sulphonamido nitrogen atoms of the methazolamidate anion at 1.999 Å distance, two pyridine nitrogen atoms at 2.053 Å distance in equatorial sites and two oxygen atoms at 2.509 Å distance in axial positions, from the water molecules.

Polycrystalline powder and single crystal EPR spectra were recorded with a VARIAN E-9 spectrometer equipped with standard X facilities. EPR suitable single crystal showing well developed faces, was oriented with an ENRAF NONIUS DELFT 586 diffractometer.

The room temperature powder EPR spectrum of the  $[\text{Cu}(\text{macm})_2(\text{Py})_2(\text{OH}_2)_2]$  exhibits clearly one perpendicular feature at  $g_{\perp} = 2.06$  and a very broad parallel one at  $g_{\parallel} = 2.27$ . When the temperature is lowered to 110 K the spectrum does not change. This shape of the EPR spectrum suggests that the complex contains grossly misaligned tetragonal axis [7].

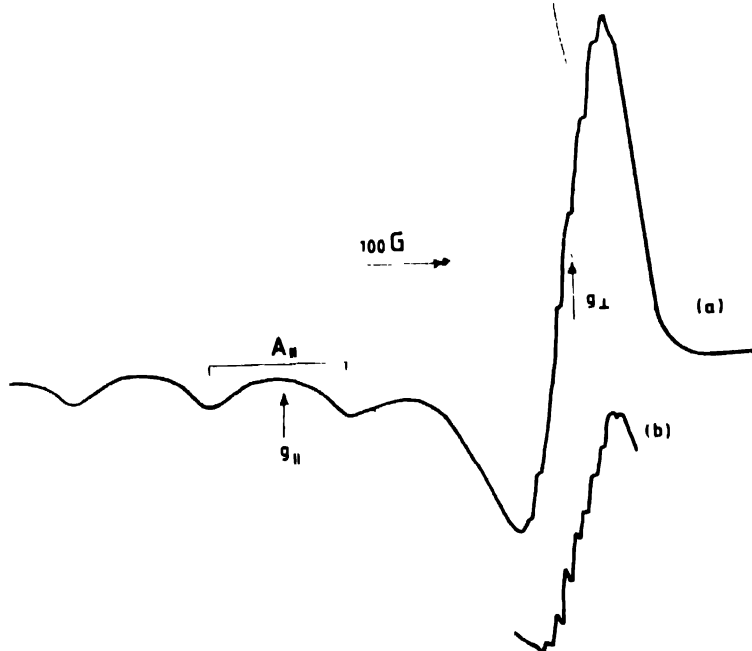


Figure 1. EPR spectra of  $[\text{Cu}(\text{macm})_2(\text{Py})_2(\text{OH}_2)_2]$  in (a) 20  $\text{mg}/\text{cm}^3$  and (b) 10  $\text{mg}/\text{cm}^3$ , DMSO solutions at 77K.

The EPR spectra of the compound, recorded in DMSO solutions at liquid nitrogen temperature, display the copper hyperfine pattern ( $g_{\parallel} = 2.27$ ,  $g_{\perp} = 2.06$ ,  $A_{\parallel} = 161.10^{-4} \text{ cm}^{-1}$ ,  $A_{\perp} = 21.10^{-4} \text{ cm}^{-1}$ ). (Figure 1). The superhyperfine lines due to the interaction of the paramagnetic electron with four equivalent nitrogen atoms ( $a^{\text{N}} = 14.5.10^{-4} \text{ cm}^{-1}$ ) appear also in the  $g_{\perp}$  region of the spectra. These lines are well resolved in the solution spectrum of 10  $\text{mg}/\text{cm}^3$  concentration (Figure 1b).

The copper(II) ion has thus a significantly elongated tetragonal-octahedral geometry. This local symmetry is confirmed also by the electronic spectrum of the studied compound which shows a broad band centred at  $17000\text{ cm}^{-1}$  and a shoulder at about  $13200\text{ cm}^{-1}$ . These absorption bands may be assigned to the  $d-d$  transitions between  $B_{1g} - E_g$  and  $B_{1g} - B_{2g}$  states respectively.

Using the appropriate LCAO-MO scheme [8,9] we have obtained the following values for the bonding coefficients:  $\alpha^2 = 0.79$ ,  $\beta^2 = 0.67$ ,  $\delta^2 = 0.75$  indicating an appreciable covalent degree for both  $\sigma$ - and  $\pi$ - bonds of the copper(II) ion with the four nitrogen atoms of the ligands.

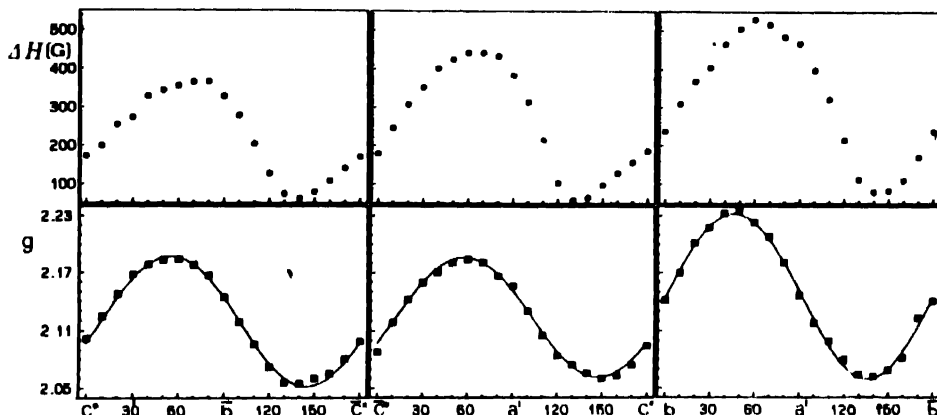


Figure 2. Angular dependence of the transition fields for  $[\text{Cu}(\text{macm})_2(\text{Py})_2(\text{OH})_2]_2$  in the three orthogonal  $b$ ,  $a' = b \times c^*$  and  $c^* = a' \times b$  planes. The solid lines represent the calculated values.

Room temperature single crystal EPR spectrum recorded at X-band frequency with the magnetic field in the  $b$ ,  $a' = b \times c^*$  and  $c^* = b \times a'$  crystal axes direction, shows only one signal for every crystal orientation in agreement with the triclinic space group. The angular dependence of the  $g$  and of the linewidth are reported in Figure 2. The components of the  $g$  tensor were obtained by the standard fitting procedure reported in [10]. The following values were obtained:  $g_1 = 2.27$ ,  $g_2 = 2.06$  and  $g_3 = 2.05$ . The direction of  $g_1$  makes an angle of  $4.2^\circ$  with O-Cu-O axis. The  $g_2$  and  $g_3$  directions are dispersed in the  $\text{CuN}_2\text{N}_2$  plane.  $g_2$  makes an angle of  $26.7^\circ$  with the Cu-sulphonamidato nitrogen atoms bond direction and  $g_3$  an angle of  $30.9^\circ$  with Cu-pyridine nitrogen atoms bond direction. The  $g$  values are as expected for a tetragonal copper compound [11]. The relatively large value for a  $\text{CuN}_2\text{N}_2\text{O}_2$  chromophore is justified for the relatively low energy of  $d-d$  transitions in the electronic spectrum [10].

The linewidth essentially follows the same pattern as the  $g$  values, i.e. it is maximum parallel to  $g_1$ . Since in an octahedral complex it is expected that the metal hyperfine splitting is much larger parallel to the tetragonal axis, it can be safely assumed that the linewidth is determined by the unresolved hyperfine structure. The fact that the lines become broader than

500G is an indication of weak inter-molecular exchange interaction, comparable to the hyperfine splitting [12].

The interpretation of the single crystal EPR spectrum permits us to explain the powder EPR spectrum in relation with the crystal structure.

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